



Biodegradation Behavior of PVA/Corn Starch Blend Films under the Influence of α -amylase Solution Immersion, Soil Burial and Water immersion

Harith I. Jaafar, Kawakib J. Majeed, Mohanad I. Kamil*

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Abstract

The objective of this work is to study the influence of α -amylase enzymatic solution immersion, soil burial and water immersion on the biodegradability behavior of polyvinyl alcohol (PVA) /Corn Starch (CS) blend films. Polyvinyl alcohol (PVA) /Corn Starch (CS) blend films were prepared by solution casting method with different weight percentages of PVA (0%, 10%, 30%, 50%, 70% and 90%). The biodegradability of the films has been investigated by determination the weight loss of the tested films. It was noticed that the films containing corn starch were highly biodegraded under above influences. The weight loss of the tested films decreased with increasing PVA content and increased with immersion time in enzymatic solution and water and soil burial time.

Key words: Biodegradation, PVA /Corn Starch, enzymatic solution immersion, soil burial, water immersion.

سلوك تحلل أفلام خليط بولي فريزل الكحول/نشأ الذرة تحت تأثير الغمر في محلول الفا ايملايز و الدفن في التربة والغمر في الماء

حارث إبراهيم جعفر، كواكب جاسم مجيد و مهند ارزوقي كامل*

قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

الهدف من هذا العمل هو دراسة تأثير الغمر في محلول الفا ايملايز والدفن في التربة والغمر في الماء على سلوك التحلل الإحيائي لخلائط بولي فينيل الكحول (PVA)/ نشأ الذرة (CS). حضرت خلائط PVA/CS باستخدام طريقة الصب اليدوي بنسب مختلفة من PVA (0% و 10% و 30% و 50% و 70% و 90%). تم التحقق من قابلية التحلل الإحيائي للخلائط من حساب الخسارة في الوزن تحت تأثير المؤثرات اعلاه. وقد لوحظ ان مقدار الخسارة في الوزن تقل مع زيادة محتوى PVA وتزداد بزيادة مدة الغمر بالمحلول الانزيمي والماء وكذلك مدة الغمر بالتربة.

Introduction

Synthetic polymers are common applications on daily used products as alternatives to costly materials such as steel, aluminium, paper and glass. Some of these polymers, such as polystyrene (PS), polypropylene (PP), and polyethylene (PE) used widely for packaging products in addition to use in the fields of biomedicine and agriculture. The main characteristics of these materials are its convenient and low cost, light weight, durability and ease of production [1].

*Email: mohanad.irzooqi@yahoo.com

Millions tonnes of synthetic polymers are produced worldwide each year, these polymers are extremely stable, and do not readily enter into the degradation cycles of the biosphere. Environmental pollution by synthetic polymers, such as waste plastics and water-soluble synthetic polymers in wastewater has been recognized as a large problem. In order to support continued sustainable development throughout the world, this problem must be addressed. In view of this, the biodegradation of plastics has been studied extensively for the past three decades. Some types of plastic have been shown to be biodegradable, and their degradation mechanisms have progressively become clearer [2].

To solve the problem caused by synthetic polymer materials, a great deal of attention has been given to the development of various biodegradable materials to overcome this serious problem, one solution is to make plastics using biodegradable polymers, which are degraded in the soil, activated sludge, or compost after the service life is over. Thus, enhancing the biodegradability is an important issue for industrial applications of biodegradable polymers [3]. However, biodegradable polymers can be defined as materials of scientific and technological interest and their use in several applications has been proposed to solve environmental problems [4-6].

Starch is one of the natural biopolymers most widely used to develop environmentally-friendly materials to substitute for petrochemical-based, non-biodegradable plastic materials [1].

Being an inherently biodegradable, renewable, and low cost material, starch has a high potential in various applications. However, wide applications have been limited due to the lack of a water barrier property and poor mechanical properties, such as film brittleness caused by high intermolecular forces. Therefore, many attempts have been made to overcome these problems by blending starch with other biodegradable synthetic polymers for numerous applications [7]. Among these polymers is polyvinyl alcohol (PVA) because it is well known as a synthetic biodegradable polymer and possesses excellent mechanical properties. Its biodegradability in various microbial environments has been reported, and PVA is one of the best options to be blended with starch. Much interest lies in blending starch with PVA because starch/PVA blends have demonstrated excellent compatibility [8]. However, the physical properties such as the mechanical properties and water resistance of the PVA/starch blended films are still lower than those of other polymers made from petroleum [1].

Experimental

Materials

The raw materials used to prepare the samples are; Corn starch powder, supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China), Polyvinyl alcohol (PVA) water-soluble powder of molecular weight (MW14000) and purity 99.9%, supplied by Merck Schuchardt OHG. Hohenbrunn, Germany, Formaldehyde and glycerine of analytical grade, were used as received from the local market. The water used was distilled and deionized water.

Preparation of the Films

Starch and polyvinyl alcohol were blended with different weight percentages of PVA (0%, 10%, 30%, 50%, 70% and 90%) by solution casting method. To get good and stable mixture, the different weight percentages of starch and polyvinyl alcohol were mixed with the water-glycerin mixture by a shearing mixer at 500 rpm for two hours to have good distribution for the mixture. The temperature of the mixture was raised to 80°C during the mixing stage. 20% weight percentage of formaldehyde was added to the mixture as plasticizer. Then the temperature of the mixture was raised to 95°C during the mixing stage for four hours. The resulting mixture was poured on a waxed glass plates for casting the blend sheets. The wax was applied to prevent the adhesion of composite sheets with glass plates. Then the samples were heated in an oven at 50°C for six hours for drying, and then the temperature was raised to 80 °C for one hour to get crosslinking.

Enzymatic Test

The enzymatic degradation test was performed by using an enzymatic mixture containing certain amounts of distilled water and 1% α -amylase, the mixture was placed in a conical flask. The dried samples were cut into dimensions $2 \times 2 \text{ cm}^2$, then the samples were weighed accurately using a digital balance of accuracy 10^{-4} gm and immersed the enzymatic mixture. And then, it was stirred with low speed in a constant temperature water bath at 50°C, adjusting PH value of the mixture at 6.9. After enzymatic degradation for a certain time, the residue was washed with water, dried at 90°C to a constant weight and weighed. The weight loss rate was calculated from equation (1):

$$\text{Weight loss rate (\%)} = \frac{W_0 - W_1}{W_0} \times 100\% \quad \dots\dots (1)$$

Where W_0 is the weight of the sample before enzymatic degradation, W_1 is the weight of the sample after enzymatic degradation.

Soil Burial Test

Biodegradation occurs with enzymatic action and involves living organisms (micro/macro). Molecular degradation is promoted by enzymes and can occur under aerobic and anaerobic conditions, leading to complete or partial removal from the environment.

Samples of dimensions $2 \times 2 \text{ cm}^2$ were buried in a pot contains soil at a depth of 10 cm. the pot was placed in the laboratory, and the moisture of the soil was maintained by sprinkling water at regular time intervals. The excess water was drained through a hole at the bottom of the pot.

The degradation of the samples was determined at regular time intervals (7 days) by carefully removing the sample from the soil and washing it gently with distilled water to remove soil from the film. The sample was dried until a constant weight was obtained. Weight loss of the sample over time was used to indicate the degradation rate of the soil burial test. The device for outdoor soil burial test is shown schematically in figure-1.

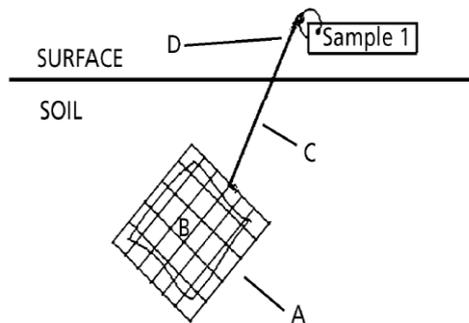


Figure 1- The scheme of the simple device for outdoor soil burial test. A = protective net; B = plastic specimen; C = wire D = sample

The soil burial test was studied by evaluating the weight loss of the film over time. The weight loss was determined every seven days from the starting day, and was calculated using equation (2):

$$\text{Weight loss rate (\%)} = \frac{W_i - W_d}{W_i} \times 100\% \quad \dots\dots (2)$$

Where W_d the dry weight of the film is after being washed with distilled water, and W_i is the initial dry weight of the specimen.

Water Immersion Test

Water gain of the immersed films was determined based on data obtained from simple immersion test using the following procedure; the samples were immersed in distilled water free of any admixture or any other wetting agent for 240 minutes to find the profile of water uptake. The test was performed under ambient temperature. The immersed samples were frequently removed from water and weighted and then replaced again in the water bath to monitor the water uptake until the film reached equilibrium weight, a Sartorius analytical balance of accuracy 10^{-4} gm was used to weight the samples, The water content (M_t) absorbed by each sample at time t was calculated by equation (3).

$$M_t (\%) = \frac{M_t - M_0}{M_0} \times 100\% \quad \dots\dots (3)$$

where M_t and M_0 are the weights of the sample after and before soaking in water.

From the water absorption we can determine the diffusion coefficient or diffusivity D that was calculated from the slope of moisture content M_t versus the square root of time \sqrt{t} as shown in Equation(4) :

$$D = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right) \quad \dots\dots (4)$$

where M_m is the maximum water content, and h is the thickness of the sample. Assuming the absorption process was linear at an early stage of immersion, the time was taken at the beginning of

absorption process so that the weight change was expected to vary linearly with the square root of time.

Results and Discussion

Enzymatic Testing

Enzymatic biodegradation of PVA/CS blends (with 20% formaldehyde) films was studied after immersion in 1% α -amylase solution for 120 min, it was noticed that the immersion cause weight loss for all films. The variation of weight loss with starch content for the immersed films was shown in figure-2.

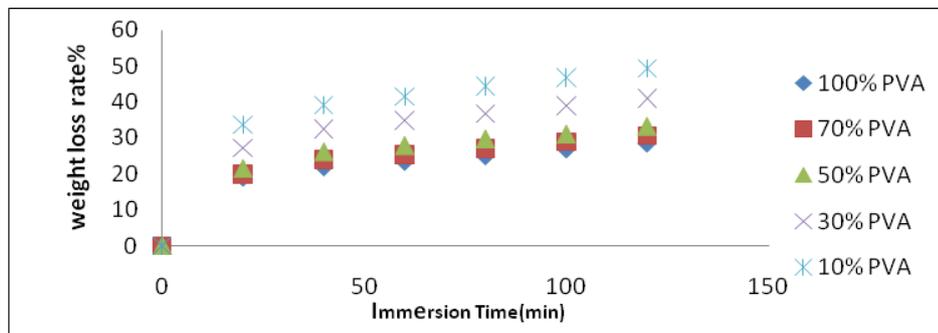


Figure 2- Variation of weight loss with PVA content and 20% formaldehyde Vs. immersion in α -amylase solution for 120 min of PVA/CS blends

It was noticed that the degradation rate of pure PVA was lower than that of PVA/starch composite films, this observation was due to the PVA/starch films absorbing more of the amylase solution than pure PVA because of the excess of -OH group in starch facilitated the penetration of α -amylase into the PVA/CS blend films and subsequently enhanced the amylase attack on the corn starch, so the films tended to absorb more of the enzymatic solution as the CS content increased [9].

For the PVA/CS blend it was observed higher degradation rate for the 10/90 weight percent PVA/CS sample, which underwent 49.26% weight loss.

However, α -amylase attacks both the main chain as well as the branch in the starch. α -amylase enzymes are endo amylases, which catalyze the hydrolysis of the internal α -1,4-glucosidic linkage in the starch in a random manner. These enzymes break down the starch into smaller sugar units, which are eventually converted to the individual basic glucose unit. The hydrolysis of the starch weakens the interaction between starch and PVA and thereby results in higher weight loss by the PVA/CS film. The corn starch also leaches out from the sample, which results in higher weight loss by PVA/CS samples due to amylase enzymes attacking the corn starch at the sample surface. This result shows that starch is more susceptible to being attacked by enzymes [10].

Soil Burial Test

After 8 weeks of soil burial, PVA/CS films with different PVA content (10%, 30%, 70%, and 100%) and 20% formaldehyde appeared brittle and fragile and diminished in size indicating the natural biodegradation of these films in the soil environment. The weight losses were probably underestimated due to soil and debris adhered to the film surface [11]. Figure-3 shows the weight loss of the pure PVA and PVA/CS films soil buried for 8 weeks.

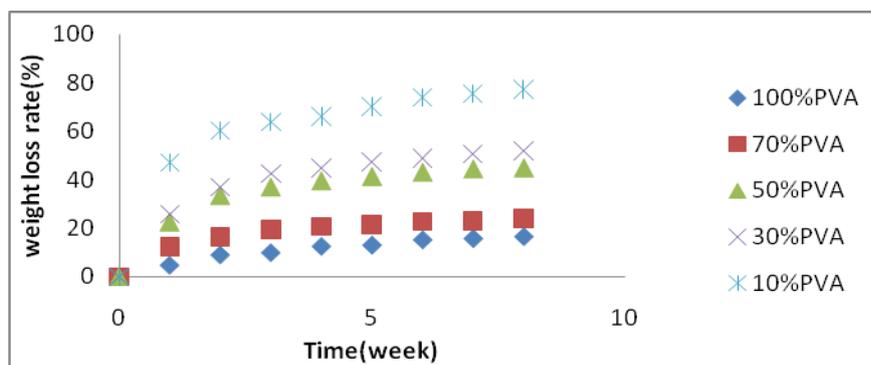


Figure 3- Weight loss rate of PVA/CS (with 20% formaldehyde) films after buried in soil for 8 weeks

From the figure-3, it can be seen that all the buried films were suffered of weight loss, the weight loss increased as the burial time increased, also it can be noticed that the weight loss decrease as the PVA content increased.

All the buried films degraded rapidly in the first 7 days. This rapid degradation was due to the composting process, which occurred in two main stages: an active composting stage and a curing period. In the first stage, the temperature rose and remained elevated as long as there was available oxygen, which resulted in strong microbial activity. In the second stage, the temperature decreased but the film continued to compost at a slower rate [12].

Figure-3, shows that the 10%PVA/90 %CS sample have the highest weight loss while pure PVA have the lowest weight loss over time. This finding was attributed to the corn starch content in the film which is more biodegradable than pure PVA. The PVA which is biodegradable due to its high hydrolysability, exhibited a higher resistance against soil burial degradation [13]. The higher weight loss for the pure PVA films was 77.19% after burial time in the soil for 8 weeks.

For the duration of 14 to 30 days the weight loss was slightly lower but the composting process did not stop at a particular point, then it continued slowly until the last remaining nutrients were consumed by the remaining micro-organisms and almost all of the carbon had been converted into carbon dioxide [12].

Water Immersion Test

Figure-4, shows the plotted curves of water gain M_t as a percentage of the original dried films against the square root of the immersion time t for PVA/CS composites (with 20% formaldehyde). It shows that the water uptake increased linearly with increasing of the square root of immersion time, then gradually slow until an equilibrium plateau is reached. This is similar to the prediction of Fickian behaviour [10]. The plateau is defined as the apparent maximum water content M_m .

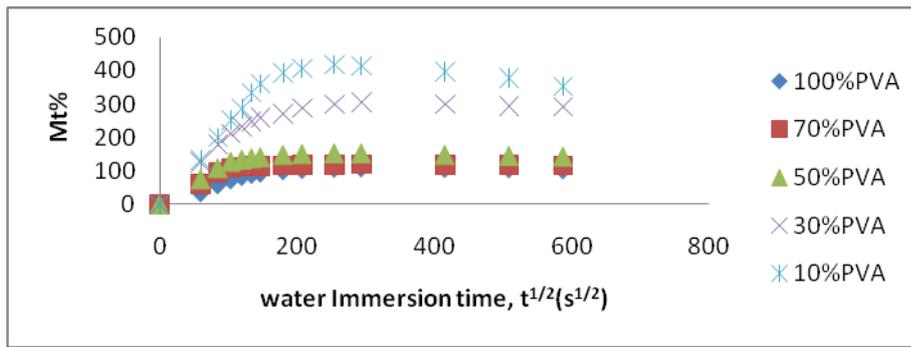


Figure 4- Weight gain M_t % as a function of square root of immersion time for the PVA/CS different PVA content and (20% formaldehyde) immersed in distilled water

PVA films that with starch demonstrated higher water uptake than the pure PVA films. Water uptake increased with increasing immersion time and starch content. This finding is due to the hydrophilic character of natural starch, which is responsible for the water absorption in the composites [12], a higher starch content led to a higher amount of water being absorbed. Water diffusion D of PVA and PVA/CS composites were calculated from the relationship between weight gain M_t and diffusivity D during initial water uptake for Fickian diffusion, figure-5, shows the variation diffusivity values (D) with PVA content for the PVA/CS blends.

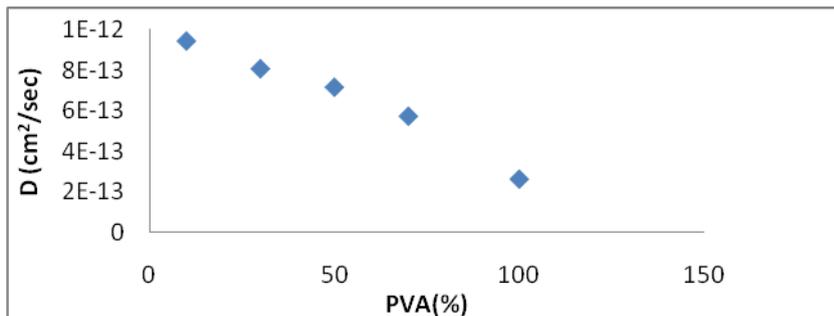


Figure 5- Variation of diffusivity values D with PVA content

As shown in figure-5, the PVA/CS films immersed in distilled water gave higher M_m values that kept increasing as the corn starch content increased. The values of M_m and D were higher in the PVA/CS blend films than in the pure PVA film; this finding is attributed to the hydrophilic nature of the PVA and corn starch due to the presence of hydroxyl groups that are available in both PVA and corn starch to interact with water molecules [9]. It was expected that the PVA/CS blend films would absorb moisture more rapidly than the pure PVA film because starch is prone to moisture and water absorption due to its hygroscopic nature. Water molecules may act as a natural plasticiser by making the starch more flexible compared to its characteristic as a hard and rigid filler in a complete dry state. Water absorption may drop slightly with increasing immersion time because some starch particles are leached away from the sample. It was expected that the starch would absorb moisture faster than pure PVA [14, 15].

Conclusions

The results obtained out of this work lead to the following : During enzymatic solution immersion, soil burial and water immersion tests ,the weight loss of CS/PVA films decrease as the PVA content increased, this finding was attributed to the CS content in the film which is more biodegradable than PVA.The water absorption of CS/PVA films followed Fick's law of diffusion. The diffusivity of the films D and the weight of the immersed films at equilibrium M_m increased as the corn starch content increased.

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